NEW PERSPECTIVES ON THE EFFECT OF HALOCARBON DEGRADATION IN OZONE FORMATION AND DESTRUCTION IN STRATOSPHERIC CHEMISTRY: THERMOCHEMICAL CONSIDERATION OF OXIDATION PROCESSES FOR TRIHALOMETHYL RADICALS

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Abstract

The fate of stratospheric trihalomethyl radicals resulting from the photo-dissociation of chlorofluoromethane, has been explored in relation to their role in reactions leading to ozone depletion. Oxidation reactions involving $CX_3O_x^{\bullet}$ radicals (X = F or Cl) are discussed from a thermo-chemical viewpoint in regards to their potential significance to atmospheric processes.

INTRODUCTION

Atmospheric chlorofluoromethanes undergo UV photodissociation in the stratosphere to yield atomic chlorine (which participates in the ClO_x catalytic cycle for ozone depletion [1]) and a trihalomethyl radical $CX_3^{\bullet}$ which is subsequently oxidised to CX_2O with the further release of a halogen atom [2]. Understanding of the mechanism of this oxidation requires knowledge of the thermodynamics and kinetics of processes involving oxygenated species $CX_3O_x^{\bullet}$ (x = 1,2 or 3). The thermochemistry of polyoxy radicals CF_3O_x was discussed in a previous paper [3] on the basis of group additivity, supported by semiempirical molecular-orbital (MO) calculations. In this paper we consider similarly the thermochemistry of $CCl_3O_x^{\bullet}$ radicals, and discuss the thermochemical feasibilities of various processes of potential atmospheric significance. In particular, the possible involvement of $CX_3O_x^{\bullet}$ species themselves in catalytic cycles for stratospheric ozone depletion is considered.

METHODS AND RESULTS

Semiempirical self-consistent-field MO calculations were carried out by the MNDO method [4] using the MOPAC and AMPAC programs [5] including parameters for chlorine [6]. Full geometry optimization was performed for each species, and open-shell systems were treated by the half-electron method [7]. Table I contains MNDO calculated heats of formation for oxygenated trihalomethyl radicals.

Thermochemical estimates for heats of formation were obtained by the group additivity method [8] using the group contribution

TABLE I

Heats of formation (kJ mol^{-1}) for
trihalomethyl polyoxy radicals calculated by the MNDO method

Compound	R = CF_3	R = CF_2Cl	R = $CFCl_2$	R = CCl_3
$R^{\bullet}$	-574	-370	-176	2
$RO^{\bullet}$	-637	-404	-203	-33
$RO_2^{\bullet}$	-657	-436	-221	-38
$RO_3^{\bullet}$	-608	-388	-176	2

ΔH_f° [O-$(O)_2$]= 55 ± 6 kJ mol^{-1} as derived previously [3]. The activation energy for dissociation of $CCl_3O_2^\bullet$ to $CCl_3^\bullet$ and molecular oxygen has been determined [9] as E_a = 94•6 ± 13 kJ mol^{-1} which, assuming a negligible barrier to recombination [10], leads to D(CCl_3 - O_2) = 97•1 ± 13 kJ mol^{-1} at 298K. Using the experimental [11] heat of formation for $CCl_3^\bullet$ then yields:

$$\Delta H_f^\circ (CCl_3O_2^\bullet) = \Delta H_f^\circ(CCl_3^\bullet) - D(CCl_3 - O_2) = -17.6 \pm 15 \text{ kJ mol}^{-1}$$

Comparison of this thermochemical estimate with the MNDO result for ΔH_f° ($CCl_3O_2^\bullet$) = -38 kJ mol^{-1} (Table I) suggests that the latter is underestimated by about 21 kJ mol^{-1}. Correcting the MNDO heat of formation for the (unknown) trichloromethoxy radical by this amount leads to $\Delta H_f^\circ(CCl_3O^\bullet)$ = -11.7 ± 21 kJ mol^{-1}. A similar procedure was used in the previous work [3] to correct the MNDO heat formation for $CF_3O_2^\bullet$, based upon a comparison of calculated and experimental values for $\Delta H_f^\circ(CF_3O^\bullet)$, and the resulting estimate for $\Delta H_f^\circ(CF_3O_2^\circ)$ was found to be consistent with experimental data. This success for the trifluoromethyl species lends support to the present method for estimation of the trichloro- methoxy heat of formation. Use of the group contribution ΔH_f°[O-$(O)_2$], as before [3], then leads to a thermochemical estimate for $\Delta H_f^\circ(CCl_3O_3\bullet)$ = 37•4 ± 15 kJ mol^{-1}; this is preferred to the MNDO value of 2 kJ mol^{-1}, which seems to be an underestimate.

Thermochemical heats of formation for the $CCl_3O_x^\bullet$ radicals considered in this work are presented in Table II along with values for other species mentioned in the subsequent discussion.

TABLE II

Thermochemical heats of formation ($kJ\ mol^{-1}$) for some chlorine containing compounds

Compound	$\Delta H_f^\circ,298$	Compound	$\Delta H_f^\circ,298$
$CCl_3^\bullet$	79.5 ± 4.2 [a]	$ClO_2^\bullet$ (asym.)	89 ± 5 [d]
$CCl_3O^\bullet$	-11.7 ± 21 [b]	$^\bullet ClO_2$ (sym.)	102 ± 3 [d]
$CCl_3O_2^\bullet$	-17.6 ± 15 [b]	$ClO_3^\bullet$ (asym.)	144 ± 9 [b]
$CCl_3O_3^\bullet$	37.4 ± 15 [b]	$^\bullet ClO_3$ (sym.)	155 [e]
$Cl^\bullet$	121.3 ± 0 [c]	$ClNO_2$	12.5 ± 1.7 [a]
$ClO^\bullet$	102.0 ± 0.8 [d]	CCl_2O	-220.1 ± 3.3 [a]

a. Ref. [11]. b. This work

c. CODATA Recommended Key Values for Thermodynamics, 1977. *J. Chem. Thermodyn.*, **10**, 903 (1978).

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DISCUSSION

Catalytic cycle for ozone destruction

Figure 1 illustrates cycles for catalytic removal of odd-oxygen species by radicals $RO_x^{\bullet}$, the simplest of which may be written as eq. (1).

(1a) $$R^{\bullet} + O_3 \longrightarrow RO^{\bullet} + O_2$$

(1b) $$RO^{\bullet} + O \longrightarrow R^{\bullet} + O_2$$

(1c) net reaction: $$O_3 + O \longrightarrow 2O_2$$

The net effect of 1a and 1b, when R = H, NO or Cl, is the destruction of ozone at a rate exceeding that of the uncatalysed reaction 1c [12]; these equations correspond to cycle 1 of Figure 1 which is entered from vertex $R^{\bullet}$ of the large triangle. Entry to cycle 2 of Figure 1 from vertex $RO^{\bullet}$ is well known [12] for RO = HO and in principle would also be possible for RO = NO_2 or ClO. Figure 1 depicts both cycles involving a species $RO_3^{\bullet}$; this is not necessarily an intermediate and may be an unbound species. Addition of O to $HO_2^{\bullet}$ (cf. cycle 2) has been shown to proceed via a bound $HO_3^{\bullet}$ intermediate [13], but dissociation to $HO^{\bullet} + O_2$ is exothermic and may involve a very low barrier (cf. ref. [3]). The existence of the chlorotrioxy radical, $ClO_3^{\bullet}$ (asymmetrical), has been suggested [14], but not demonstrated [15]. The newly derived [3] value for $\Delta H_f^{\circ}[O\text{-}(O)_2]$ allows the heat of formation for chlorotrioxy to be estimated as 144 ± 9 kJ mol^{-1}, which suggests that this species may be of lower energy than the isomeric chlorate radical, $ClO_3^{\bullet}$ (symmetrical), although kinetically it may be extremely liable towards exothermic dissociation to $ClO^{\bullet}$ and $O_2^{\bullet}$.

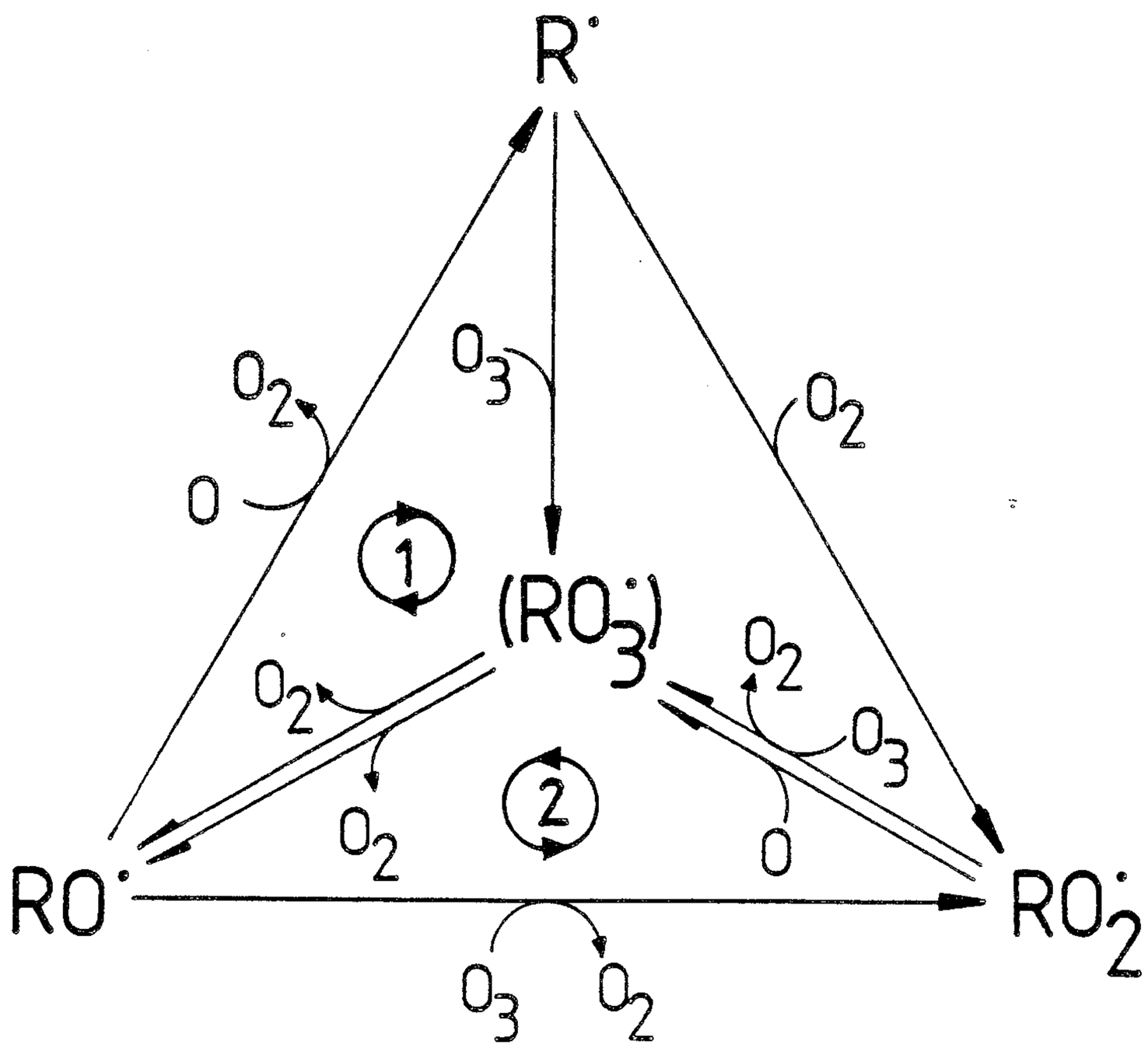

Figure 1. Catalytic cycles for odd-oxygen removal: general scheme.

$CX_3O_x^{\bullet}$ Catalytic cycles

The possible involvement of trihalomethyl radicals in the catalytic cycles shown in Figure 1 (R = CF_3, CF_2Cl, $CFCl_2$ or CCl_3) does not appear to have been previously considered. The requirements for catalysis are that each step of a cycle should be exothermic and should proceed at a rate greater than that of the uncatalysed process. The following discussion is restricted to thermochemical considerations of possible catalytic cycles involving trihalomethyl species and is presented as a general survey for the purpose of identifying reaction steps of interest for future detailed kinetic studies.

The feasibility of a potentially catalytic cycle depends also upon the availability of alternative reaction channels which may serve to remove catalytically active species. Figure 2 illustrates the possible catalytic cycles for ozone destruction involving $CX_3O_x^{\bullet}$; the numbers beside each reaction step are heats of reaction in kJ mol^{-1} for the cases X = F and (in parentheses) X = Cl. Figure 2 therefore summarizes the thermochemical data relating to the catalytic cycles of Figure 1 for the specific cases of R = CF_3 and CCl_3, but also shows possible channels for removal of the key radicals $R^{\bullet}$, $RO^{\bullet}$ and $RO_2^{\bullet}$. The carbonyl dihalide CX_2O is here regarded as an atmospheric sink (cf. the recent detection of stratospheric CF_2O [16]); actually, it is liable to photodissociation itself, leading ultimately to the production of either CO or CO_2 [17]. Reactions of $CX_3^{\bullet}$, $CX_3O^{\bullet}$ and $CX_3O_2^{\bullet}$ are now considered in turn.

$CX_3^{\bullet}$

The high exothermicities for ozonation of $CX_3^{\bullet}$ (Figure 2, X = F or Cl) almost certainly preclude the existence of $CX_3O_3^{\bullet}$ as a distinct intermediate, since its dissociation to $CX_3O^{\bullet}$ and O_2 is also exothermic

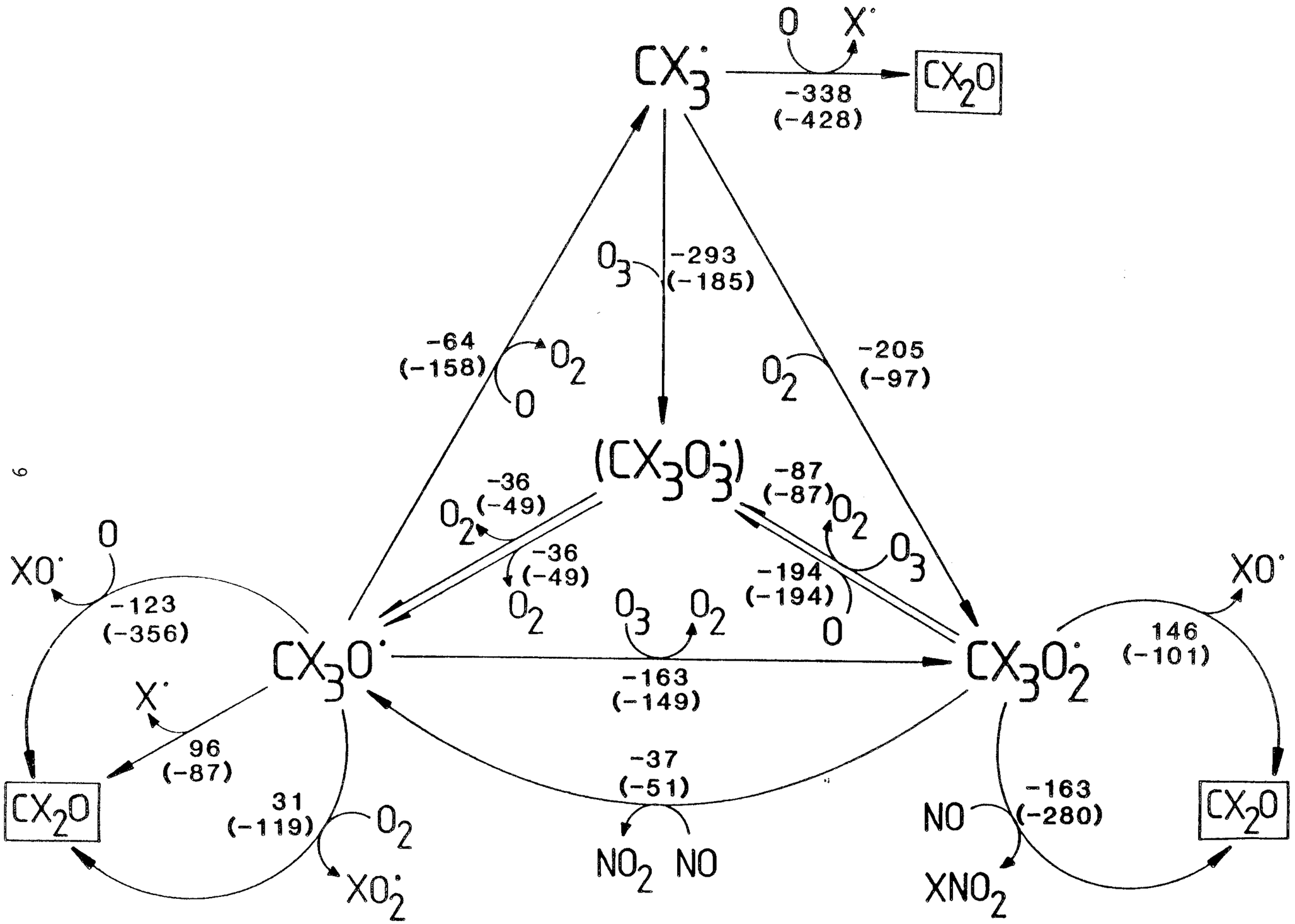

Figure 2. Heats of reaction (kJ mol^{-1}) for possible atmospheric processes involving $CX_3O_x^{\cdot}$ radicals, where X = F and (in parentheses) X = Cl.

in each case, and probably involves only a low barrier. The heat of reaction (1a) for R = CF_3 is calculated as -331 kJ mol^{-1} by the MNDO method in agreement with the thermochemical value of -328 kJ mol^{-1}. The MNDO calculated heats of reaction (1a) for R = CF_2Cl, $CFCl_2$ and CCl_3 are, respectively, -301, -294 and -263 kJ mol^{-1}, i.e. ozonation becomes less exothermic with increasing chlorination. Addition (2) of molecular oxygen to $CX_3^{\bullet}$ also becomes less exothermic with increasing chlorination. Conversely, the sink reaction (3) of atomic oxygen with trihalomethyl is more exothermic for X = Cl than for X = F.

$$(2) \qquad CX_3^{\bullet} + O_2 \xrightarrow{M} CX_3O_2$$

$$(3) \qquad CX_3^{\bullet} + O\ (^3P) \longrightarrow CX_2O + X^{\bullet}$$

The halogen atoms released by this process may themselves enter cycles for catalytic destruction of ozone. However, it is generally considered [18] that F-atom chain reactions are much shorter than Cl-atom chains, since HF generated by abstraction of hydrogen -- from, e.g., methane -- is a sink for fluorine [18] whereas HCl serves merely as a reservoir for chlorine [12].

$CX_3O^{\bullet}$

Regeneration of $CX_3^{\bullet}$ by reaction of atomic oxygen with $CX_3O^{\bullet}$ -- the second step of cycle 1 -- is in competition with a more exothermic channel, halogen abstraction yielding CX_2O and $XO^{\bullet}$. The relative rates of these processes are unknown. Hypohalite radicals $XO^{\bullet}$ are the conjugate species with halogen atoms in XO_x catalytic cycles. An alternative step (5) for regeneration of $CX_3^{\bullet}$ radicals, by self-recombination of $CX_3O^{\bullet}$ and loss of O_2, is an endothermic reaction for

$$(4) \qquad 2CX_3O^{\bullet} \longrightarrow 2CX_3^{\bullet} + O_2$$

X = F and Cl and cannot be a part of a catalytic cycle. Halogen abstraction from $CX_3O^{\bullet}$ by molecular oxygen, yielding CX_2O and $XO_2^{\bullet}$, is endothermic for X = F but endothermic for X = Cl. Similarly, dissociation of $CX_3O^{\bullet}$ to CX_2O and $X^{\bullet}$ is endothermic for X = F but exothermic for X = Cl (Figure 2). MNDO [19] and *ab initio* MO [20] results for $CX_3O^{\bullet}$ dissociation concur that loss of Cl from a mixed chlorofluoromethoxy radical is always favourable whereas loss of F is always unfavourable.

Finally, ozonation of $CX_3O^{\bullet}$ to give $CX_3O_2^{\bullet}$ and O_2 is an exothermic process for X = F and Cl; the MNDO results suggest that the heat of reaction is almost a constant for mixed chlorofluoro-species. This reaction is the first step of catalytic cycle 2 (Figure 1).

$CX_3O_2^{\bullet}$

Atomic oxygen addition to $CX_3O_2^{\bullet}$, the second step of cycle 2, yields $CX_3O^{\bullet}$ and O_2 exothermically (Figure 2) in a process formally involving $CX_3O_3^{\bullet}$ but which, as mentioned above, does not necessitate the existence of the latter as a distinct intermediate. Collisions with molecular oxygen may serve to stabilize $CX_3O_2^{\bullet}$, the dissociation of which to CX_2O and $XO^{\bullet}$ is, again, endothermic for X = F, but exothermic for X = Cl. Other channels for removal of $CX_3O_2^{\bullet}$ involve reactions with NO. Oxygen-atom abstraction yielding $CX_3O^{\bullet}$ and NO_2 is exothermic, but in each case $XO^{\bullet}$ abstraction to give CX_2O and XNO_2 as sinks is much more exothermic. The kinetics of the former process have been determined [21], whereas evidence for the latter has been obtained in low-temperature matrix studies [22].

Addition of ozone to $CX_3O_2^\bullet$ would generate $CX_3O_3^\bullet$ and O_2 exothermically. The lifetime of the trihalomethyltrioxy radical is likely to be too short to allow collisions with oxygen atoms to occur. Thus, the possibility of a third catalytic cycle, initiated by $CX_3O_2^\bullet$ may be discounted.

CONCLUSION

Thermochemical analysis of reactions of trihalomethyl species $CX_3O_x^\bullet$ (X = F or Cl, x = 0-3) suggest that, in principle, they could be involved in catalytic cycles for stratospheric ozone depletion. Trioxy radicals $CX_3O_3^\bullet$ implicated in these cycles are expected to be very transient (and possibly unbound) species. Trichloro-species $CCl_3O_x^\bullet$ tend to dissociate readily to phosgene and $Cl^\bullet$ or $ClO^\bullet$ which enter the ClO_x catalytic cycle. Trifluoro-species $CF_3O_x^\bullet$ tend to be more stable. Catalytic cycles whose first steps are ozonation of $CF_3^\bullet$ or $CF_3O^\bullet$ are potentially feasible whereas a cycle simiarly initiated by $CF_3O_2^\bullet$ is not feasible. Reactions of $CF_3O^\bullet$ and $CF_3O_2^\bullet$ respectively with atomic oxygen would complete these catalytic cycles and are, therefore, potentially significant processes which warrant studies of their kinetics. The competition of these reactions with other channels for removal of $CF_3O^\bullet$ and $CF_3O_2^\bullet$ will determine the viability of the potential $CF_3O_x^\bullet$ catalytic cycles.

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